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(71) 出願人 000217228

田中貴金属工業株式会社

東京都中央区日本橋茅場町2丁目6番6号

(71) 出願人 000218166

渡辺 政廣

山梨県甲府市和田町2421番地の8

(74) 代理人 弁理士 森 浩之

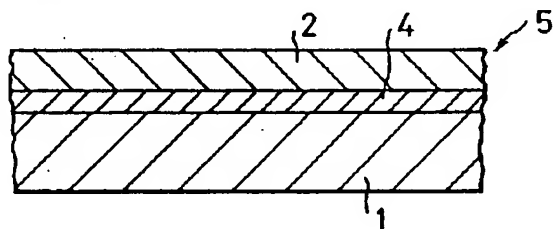
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(54) 【発明の名称】 高分子固体電解質型燃料電池用電極及びその製造方法

## (57) 【要約】

【目的】 従来の燃料電池より触媒利用率の高い燃料電池を提供する。

【構成】 ガス拡散層1と触媒層2の間に中間層4を設置した燃料電池用電極5。中間層が存在しないと触媒層の一部がガス拡散層の細孔に進入し、触媒の一部が所望反応に利用されず、更にガス拡散能を阻害して反応効率を低下させる。前記中間層の存在により、前記触媒層のガス拡散層への進入を防止して触媒利用率を向上させる。更に中間層の代わりにガス拡散層の触媒層に近接する部分の気孔率を小さくすることによっても同等の効果が得られる。又触媒層中に例えば燃料電池反応を促進する機能を有する第1の触媒金属と燃料中のCOを吸着除去する第2の触媒金属を触媒層の厚さ方向にその種類を異ならせて存在させると、両機能を好適に有する燃料電池用電極が提供できる。この電極の製造には構成原料のそれぞれの懸濁液を複数回に分けて塗布及び焼成することにより得られる。



## 【特許請求の範囲】

【請求項1】 触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂による触媒層が、ガス拡散層上に形成された高分子固体電解質型燃料電池用電極に於いて、前記触媒層とガス拡散層との間に、中間層を設けたことを特徴とする高分子固体電解質型燃料電池用電極。

【請求項2】 中間層が、カーボンとイオン交換樹脂又はカーボンとイオン交換樹脂と親水性樹脂からなるものであることを特徴とする請求項1記載の高分子固体電解質型燃料電池用電極。

【請求項3】 触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂による触媒層が、ガス拡散層上に形成された高分子固体電解質型燃料電池用電極に於いて、前記触媒層に近接する部分のガス拡散層の気孔率を10~50%としたことを特徴とする高分子固体電解質型燃料電池用電極。

【請求項4】 ガス拡散層の気孔率を触媒層側に向かって小さくしたことを特徴とする請求項3に記載の高分子固体電解質型燃料電池用電極。

【請求項5】 触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂より構成された高分子固体電解質型燃料電池用電極に於いて、触媒に用いる2種類以上の貴金属又は貴金属合金が触媒層の厚み方向で種類が異なるように配置されていることを特徴とする高分子固体電解質型燃料電池用電極。

【請求項6】 触媒層のガス拡散層側に白金及び／又はルテニウム触媒が配置され、触媒層の膜側に白金系合金触媒が配置され、アノードとして使用されることを特徴とする請求項5に記載の高分子固体電解質型燃料電池用電極。

【請求項7】 触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂よりなる高分子固体電解質型燃料電池用電極の製造方法に於いて、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂を含む懸濁液を、ガス拡散層上に塗布し、乾燥し、焼成することを複数回繰り返して触媒層を形成することを特徴とする高分子固体電解質型燃料電池用電極の製造方法。

【請求項8】 ガス拡散層上に繰り返して塗布する懸濁液の少なくとも1つが、異なる混合比率で構成された懸濁液であることを特徴とする請求項7に記載の高分子固体電解質型燃料電池用電極の製造方法。

【請求項9】 電極基板上に繰り返して塗布する懸濁液の少なくとも1つが、異なる原料を用いて構成された懸濁液であることを特徴とする請求項7に記載の高分子固体電解質型燃料電池用電極の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、高分子固体電解質型燃料電池用電極及びその製造方法に関し、より詳細には触媒層とガス拡散層から成る燃料電池用電極における

前記触媒層の触媒の利用効率を向上させた前記燃料電池用電極及びその製造方法に関する。

## 【0002】

【従来技術及び問題点】燃料電池は、水素や各種化石燃料を用いる高効率、無公害発電装置であることから、エネルギー問題、全地球的公害問題に対処できる、“ポスト原子力”の発電装置として、社会的に大きな期待が寄せられている。火力代替発電用、ビルディングや工場単位のオンサイト発電用、あるいは宇宙用など、用途に応じた各種燃料電池が開発されている。近年、炭酸ガスを中心とする温室効果や、NOx、SOx等による酸性雨が地球の将来を脅かす深刻な公害として認識されてきた。これら公害ガスの主要な排出源の一つが自動車等の内燃機関であることから、燃料電池を車載用内燃機関に代えて作動するモータ電源として利用する気運が急速に高まりつつある。この場合、多くの付帯設備と同様、電池は可能な限り小型であることが望ましく、そのためには電池本体の出力密度、出力電流密度が高いことが必須である。この条件を満たす有力な燃料電池の候補として、イオン交換膜を用いた高分子固体電解質型燃料電池（以下PEMFCという）が注目されている。

【0003】燃料電池の電極3は、図3に示すように例えば炭素質材料から成るガス拡散層（電極基板）1上に、触媒を担持したカーボンブラックや炭素繊維から成る担体を水や有機溶媒に懸濁したペーストを塗布して触媒層（反応層、電極触媒層）2を形成することにより製造されている。燃料電池の反応は前記触媒上で起こるため、どのようにして前記触媒を有効利用するかが、前記燃料電池により得られるエネルギー量を左右する最大の要因である。しかしながら従来の燃料電池では種々の理由により触媒の利用効率を最大にすることができず、高価な触媒特に白金族金属触媒を有効利用できていないという欠点がある。本発明者らはこの燃料電池の触媒層中に存在する触媒の有効利用が図れない理由を熟慮した結果、次の3点が主要な理由であるとの結論に達した。

【0004】その第1の理由は、従来のガス拡散層の気孔率が約60~80%と高いため、触媒層のガス拡散層に面し又は近接する部分に存在する触媒を含む触媒層が電極形成の際にガス拡散層中へしみ込みあるいは進入し、触媒の一部が実質的にガス拡散層中に存在することであり、この触媒はプロトンの導伝が難しくなり、その結果該触媒は反応には寄与できず、触媒の利用率が低下する。第2の理由として、触媒層中に存在する触媒が1種類であることが挙げられる。例えばPEMFCはその低温運転性のため、アノード電極の触媒が燃料中のCOにより被毒され易いという問題点があり、従来から各種合金触媒が提案され、耐CO被毒性を有する燃料電池用触媒の実用化が試みられているが、いずれも不十分である。

【0005】第3の理由として、触媒層の触媒濃度が均

一であることが挙げられる。従来から高分子固体電解質型燃料電池用電極の触媒層は、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂を、有機溶媒と水との混合液に懸濁した懸濁液を、電極基板上に一度に塗布し、乾燥し、焼成を行なって製造されている。この方法では一度に塗布を行なうため、触媒層の厚み方向で、触媒層の混成原料を変えることができず、触媒層の厚み方向でそれぞれに応じた最適な触媒層を得ることができない。燃料電池の反応はガス拡散層と触媒層の界面でその殆どが生じ、従来の触媒層中の触媒が均一に分散する燃料電池の触媒層では、ガス拡散層から遠く位置する触媒は殆ど前記反応に寄与できず触媒利用率が低下している。更にこの方法では、一度に懸濁液を電極基板上に塗布するため、触媒層が厚くなり乾燥の途中で大きなクラックが入ることがあるという欠点を有している。

#### 【0006】

【発明が解決しようとする課題】そこで本発明は、第1に触媒層中の触媒がガス拡散層中に進入してその触媒活性を失うことのない高分子固体電解質型燃料電池用電極を提供する。本発明は、第2に耐CO被毒性を有しかつ燃料電池の反応に対しても活性を有する高分子固体電解質型燃料電池用電極を提供する。本発明は、第3に触媒層の厚み方向に応じた活性を有する高分子固体電解質型燃料電池用電極を提供する。

#### 【0007】

【課題を解決するための手段】上記の課題を解決するための本発明の第1の態様は、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂による触媒層が、ガス拡散層上に形成された高分子固体電解質型燃料電池用電極に於いて、前記触媒層がガス拡散層中にしみ込みあるいは進入しないように触媒層とガス拡散層との間に、中間層を設けたことを特徴とする高分子固体電解質型燃料電池用電極である。本発明の第2の態様は、同様の高分子固体電解質型燃料電池用電極に於いて、触媒層が近接する部分のガス拡散層の気孔率を10~50%としたことを特徴とする高分子固体電解質型燃料電池用電極である。

【0008】本発明の第3の態様は、同様の高分子固体電解質型燃料電池用電極に於いて、触媒として使用される2種類以上の貴金属又は貴金属合金の種類が電極の厚み方向で種類が異なるように配置されていることを特徴とする高分子固体電解質型燃料電池用電極、特にアノード用電極である。本発明の第4の態様は、同様の高分子固体電解質型燃料電池用電極に於いて、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と親水性樹脂を、有機溶剤と水等との混合液に懸濁した懸濁液を、電極基板上に塗布し、乾燥し、焼成することを複数回繰り返して電極触媒層を形成する高分子固体電解質型燃料電池用電極の製造方法である。

【0009】以下本発明を詳細に説明する。前記第1の

態様及び第2の態様はいずれも、触媒層中の触媒がガス拡散層中に進入して触媒活性を失うことを防止しようとするものである。前述した通り、触媒層中の触媒は触媒層中に存在して初めて燃料電池反応を促進する触媒効果を生ずるのであり、ガス拡散層中に存在するとガス拡散を阻害して前記触媒層への反応ガスの供給及び生成ガスの排出を妨害する機能しか有しない。従って触媒層中に存在する触媒あるいは触媒層自身のガス拡散層中への進入を防止できれば確実に触媒の利用率は向上する。そのため本発明では触媒層に接するガス拡散層の気孔率を低くして触媒の進入を抑制するか、あるいは前記触媒層がガス拡散層中にしみ込まないようにあるいは進入しないように触媒層とガス拡散層との間に中間層を形成する。

【0010】通常の燃料電池のガス拡散層の気孔率は約60~80%であるが、本発明ではこの気孔率を10~50%と低くすることにより、ガス拡散層に形成される孔径を小さくして触媒層が進入しないようにする。気孔率を10~50%とした理由は、10%未満ではガス拡散層の本来の機能であるガス拡散機能が損なわれて反応ガスの供給及び生成ガスの排出が円滑に行なえなくなるため、逆に反応を阻害することになるからであり、50%を超えると通常のガス拡散層の気孔率は殆ど同等になり、前記触媒の進入防止の改善効果が少ないからである。この触媒の進入防止はガス拡散層の触媒層に接する比較的僅かな厚さの部分のみで行なわれれば十分であり、ガス拡散層の気孔率を、触媒層側に向かうほど小さくする等してガス拡散層のガス拡散能力が損なわれないようにすることが好ましい。

【0011】前記気孔率の大小は、ガス拡散層製造時のホットプレスの条件等により調節することができ、気孔率の小さいガス拡散層を製造するためにはホットプレスの圧力を大きくすれば良い。触媒層に向かうほど気孔率が小さくなったガス拡散層を製造するには、例えば気孔率を異なる薄厚のガス拡散層を複数枚準備しそれらを互いに接合すれば良い。次に前述の中間層を設けるのは、該中間層に、気孔率を小さくした上述のガス拡散層の少なくとも触媒層に近接する部分と同等の機能を果たさせるためである。該中間層にも触媒層が進入しないようにその気孔率は小さくすることが望ましいが一部が進入してもさほど反応低下には結びつかず、中間層は触媒層とガス拡散層が直接接触することを防止できればその機能が達成され、該中間層の気孔率は10~80%程度の広い範囲とすることができ、20~60%程度が望ましい。該中間層の気孔率が仮に80%であっても触媒層が直接ガス拡散層に進入しないため、該中間層の存在によりガス拡散層へ進入する触媒層の割合が大きく減少し、触媒の利用率向上に貢献する。

【0012】前記中間層の材質はガス拡散層の材質と同様にしても、類似する性質を有する他の材質でも良く、

カーボンとイオン交換樹脂又はカーボンとイオン交換樹脂と撈水性樹脂からなるものであることが好ましい。本発明の第1及び第2の態様では、燃料電池の触媒層中の触媒がガス拡散層に進入して実質的な触媒量が減少することが殆どなく、その有効利用を図ることができる。本発明の第3の態様では、触媒層を構成する貴金属又はその合金を2種類以上使用することにより触媒層の触媒の性能を最大限活用することにより触媒利用率を向上させることを意図している。同じ触媒層に存在する触媒でもその存在位置によりその機能が異なる場合がある。燃料電池の電極特にアノードでは、電極触媒には燃料電池の反応を促進する機能と、燃料中に混入して前記触媒に供給されアノードを被毒してアノードの反応活性を低下させるCOを吸着して燃料中から除去するという機能がある。

【0013】例えば燃料電池反応の触媒としては白金系合金が、CO吸着用としては白金触媒やルテニウム触媒が好ましい。従来の燃料電池用電極の触媒層には1種類の貴金属又はその合金のみがほぼ均一に分散され、燃料電池反応に有効かつCOの吸着除去にも有効である1種類の貴金属合金触媒が探究されてきたが、両機能とも満足する貴金属合金触媒は見出されていない。本発明の前記第3の態様では、この1種類の貴金属又は貴金属合金触媒による2種類以上の機能の達成という従来の基本的な考え方から離れ、各機能に対する最適の貴金属又は貴金属合金触媒を複数併用することにより各機能を全て満足できる燃料電池用触媒特にアノード触媒を提供する。

【0014】例えば燃料電池反応の促進と燃料中のCOの吸着除去の両機能の達成を意図する燃料電池用アノードの場合には、触媒層のうちガス拡散層に近い側に白金触媒又はルテニウム触媒を用いてこの触媒層において主として吸着燃料中のCOの吸着除去を行ない、触媒層のうち膜に近い側に白金系合金触媒を用いてこの触媒層において燃料電池反応を促進するようにする。つまり燃料はアノードのガス拡散層を通して触媒層に供給され該触媒層の前記ガス拡散層と反対側の膜の近傍で水素ガスの酸化反応が起こり、同じ触媒層でもガス拡散層に近い部分は膜近傍で起こる水素ガスの酸化反応にさほど寄与している訳ではない。従ってこの触媒層中のガス拡散層に近い部分の触媒金属を水素ガス酸化にはさほど有効ではないがCOの吸着除去には効果的な例えば前述した白金やルテニウムを担持すると、アノード全体の触媒効果を殆ど減少させることなく、アノードに供給される燃料中のCOを除去できるという相乗効果が生ずる。つまり燃料に伴ってアノード電極に供給されるCOは先ず白金触媒又はルテニウム触媒に吸着し易いために、これに吸着する。ここで吸着平衡に達すると、白金系合金の触媒へと吸着が進むが、白金触媒又はルテニウム触媒の領域でのフィルター効果により白金系合金等の膜に近い側の触

媒まで到達するCOが減少し、CO被毒の割合が低減する。従って、膜に近い側の燃料電池反応を促進する触媒の性能を低下させることなく耐CO性に優れた電極となる。

【0015】前述した使用する貴金属又は貴金属合金の種類は2種類以上で限定はないが通常は2種類とし、又アノード以外にカソードを同様に構成するようにしても良い。又前記2以上の貴金属又は貴金属合金は層状に、つまり触媒層の厚さ方向に複数の貴金属又は貴金属合金が存在するように配置する。なお金属間界面は厳密に区画されている必要はなく、界面付近で2種類以上の貴金属又は貴金属合金が混在していても良い。前記2種類以上の貴金属又は貴金属合金を含む触媒層は、1種類の貴金属又は貴金属合金を含む触媒層前駆体を複数枚作製しこれらを接合することにより、又は予め作製した貴金属又は貴金属合金のみを含む第1の触媒前駆体の表面に他の貴金属又は貴金属合金を含む懸濁液を塗布し焼成して第2の触媒前駆体を形成すること等により製造できる。

【0016】本発明の第4の態様は高分子固体電解質型燃料電池用電極の製造方法に係わり、大きなクラックのない触媒層、あるいは触媒層を構成する貴金属又はその合金を層の厚さ方向に2種類以上使用し、又は1種類の貴金属又は貴金属合金の層の厚さ方向の濃度を変化させた触媒層の製造に適している。従来の燃料電池の触媒層は、ガス拡散層上に、触媒を担持した担体とフッ素樹脂等を混練した懸濁液を一度に塗布し焼成することにより製造されるが、この方法ではガス拡散層上に一度に塗布する懸濁液量が多くなり、焼成時や乾燥時の収縮による歪みが大きくなり、大きなクラックが生じ易く、燃料電池として使用した際の液漏れやガス漏れに結び付き易い。一方本発明のように懸濁液を複数回に分けて塗布し焼成を行なうと1回に塗布する懸濁液の量が少なくなり、その膜厚が薄くなる為、乾燥時の収縮による歪みが小さく、従って大きなクラックが入りにくく、均一で歪みのない触媒層を製造できる。

【0017】又異なる混合比率（組成）又は原料を用いた懸濁液を複数回塗布することにより、得られる電極触媒層の厚み方向に要求されるさまざまな機能を備えさせることができる。例えば、膜側に触媒を多く配置したり、イオン交換樹脂を多く配置したりすることができ、その結果、触媒の有効利用やプロトンの導伝及びガス拡散機能が向上し、電極特性に優れたものとなる。更に例えば前述した本発明の第3の態様である複数の貴金属又は貴金属合金を有する触媒層の製造にも有用である。塗布する回数は2回以上6回程度が望ましく、6回を超えるとより以上の効果が望めない反面、作業性が悪く、コスト高となるからである。

【0018】

【実施例】本発明の高分子固体電解質型燃料電池用電極及びその製造方法の実施例を比較例とともに説明する

が、これらは本発明を限定するものではない。

【比較例1】Pt 50%担持触媒2gとイオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液20gと蒸留水6gを遊星ボールミルにて50分間混合して得たペーストを、バーコート法にて気孔率80%の図3に示すガス拡散層1へ塗布し、60℃で10分間乾燥し、更に130℃、20kg/cm<sup>2</sup>で1分間焼成して触媒層2を形成し電極3を得た。

【0019】

【実施例1】比較例1と同じ触媒層2とガス拡散層1とよりなる電極に於いて、予め触媒層2とガス拡散層1との間に、図1に示すようにカーボン2gとイオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液15gと蒸留水10gを遊星ボールミルにて50分間混合して得たペーストを介在させ、換言すると該ペーストをガス拡散層1へ塗布し、60℃、10分間乾燥し、130℃、20kg/cm<sup>2</sup>で1分間焼成して中間層4を形成し、然る後この中間層4の上に前記触媒層2を形成して電極5を得た。

【0020】上記のように製造された比較例1の電極と実施例1の電極を用いて、セル温度80℃、2気圧の水素ガスと3気圧の酸素ガスの条件で、電圧と電流密度の関係を測定したところ、図5のグラフに示すような結果を得た。このグラフで判るように実施例1の電極（Ec）は、比較例1の電極（Ea）よりも電極特性が優れていることが判る。これは実施例1の電極が、ガス拡散層に中間層の存在により触媒層がしみ込まず、触媒量が減少せず、触媒が有効利用できたからであると推測できる。

【0021】

【比較例2】Pt 30%担持触媒1.43gとイオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液10gと蒸留水4gを、遊星ボールミルにて50分間混合して得たペーストを、バーコート法にて気孔率80%の図4に示すガス拡散層1へ塗布し、60℃、10分間乾燥し、130℃、20kg/cm<sup>2</sup>で1分間焼成して触媒層2'を形成し、電極3'を得た。

【0022】

【実施例2】比較例2と同じペーストをバーコート法にて気孔率約33%の図2に示すガス拡散層1'へ塗布し、60℃、10分間乾燥し、130℃、20kg/cm<sup>2</sup>で1分間焼成して触媒層2'を形成し、電極6を得た。上記のように構成された比較例2の電極と実施例2の電極を用いて、セル温度80℃、水素ガスと酸素ガスを常圧の条件で、電圧と電流密度の関係を測定したところ、図6のグラフに示すような結果を得た。このグラフで判るように実施例2の電極（Ed）は、比較例2の電極（Eb）よりも電極特性が優れていることが判る。これは実施例2の電極が、目詰まり状態のガス拡散層に触媒層がしみ込まず、触媒量が減少せず、触媒が有効利用できたからであると推測できる。

【0023】

【比較例3】Pt 30%担持触媒1.43g、イオン交換樹脂

（商品名ナフィオン）5%溶液の濃縮液10g、蒸留水4gを遊星ボールミルにて粉碎、攪拌、混合してペーストを作り、このペーストをカーボンペーパーの電極基板上に塗布し、乾燥し、焼成して、40μmの触媒層を形成し、アノード電極を得た。

【0024】

【比較例4】Pt-Mo 33%担持触媒 1.5g、ナフィオン5%溶液の濃縮液10g、蒸留水4ccを遊星ボールミルにて粉碎、攪拌、混合してペーストを作り、このペーストをカーボンペーパーの電極基板上に塗布し、乾燥し、焼成して、40μmの触媒層を形成し、アノード電極を得た。

【0025】

【実施例3】Pt 30%担持触媒1.43g、イオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液10g、蒸留水4ccを遊星ボールミルにて粉碎、攪拌、混合して第1ペーストを作り、またPt-Mo 33%担持触媒 1.5g、イオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液10g、蒸留水4ccを遊星ボールミルにて粉碎、攪拌、混合して第2ペーストを作り、そして第1ペーストをカーボンペーパーの電極上に塗布し、乾燥し、焼成して10μmの第1触媒層を形成し、その上に第2ペーストを塗布し、乾燥し、焼成して30μmの第2触媒層を形成して、アノード電極を得た。

【0026】これら比較例3、4及び実施例3のアノード電極を、セル温度80℃で、CO 100ppmを含む水素ガスと酸素ガスをそれぞれ1リットル/min、常圧にて供給し、電圧と電流密度との関係を測定したところ、図7のグラフに示すような結果を得た。図7のグラフで判るように実施例3のアノード電極は、比較例3、4のアノード電極よりも電極特性に優れていることが判る。これは実施例3のアノード電極が、第1触媒層でCOが吸着され、第2触媒層に到達するCOが減少し、CO被毒の割合が低減して耐CO性に優れた電極となったからであると推測できる。

【0027】

【比較例5】Pt 30%担持触媒1.43gとイオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液10gと蒸留水4gを遊星ボールミルにて50分間攪拌混合してペーストを作り、このペーストをカーボンペーパーの電極基板上に1度で1mg/cm<sup>2</sup>のPt担持量となるように印刷し、乾燥し、焼成して、高分子固体電解質型燃料電池用電極を得た。

【0028】

【実施例4】比較例5と同じペーストを作り、このペーストをカーボンペーパーの電極基板上に3回に分けて印刷し、乾燥し、焼成して、Pt 1mg/cm<sup>2</sup>の担持量の触媒層を形成し、高分子固体電解質型燃料電池用電極を得た。

【0029】



【実施例5】Pt 30%担持触媒1.43gとイオン交換樹脂（商品名ナフィオン）5%溶液の濃縮液6gと蒸留水7gを遊星ボールミルにて50分間攪拌混合して第1ペーストを作り、また比較例5と同じペーストとを第2ペーストとして作り、これら第1ペースト、第2ペーストをカーボンペーパーの電極基板上に2回ずつ計4回印刷し、乾燥し、焼成して、触媒層を形成し、高分子固体電解質型燃料電池用電極を得た。

【0030】これらの高分子固体電解質型燃料電池用電極を検査したところ、比較例5のものは、部分的な剥離があったが、実施例4、5のものは剥離がなく大きなひびも全くなかった。これらの高分子固体電解質型燃料電池用電極の電圧と電流密度との関係をセル温度80℃、水素ガスと酸素ガスをそれぞれ1リットル/min、常圧の条件で測定したところ、比較例5のものは全く測定できず、実施例4及び実施例5のものは図8のグラフに示すような結果を得た。図8のグラフで判るように実施例5の高分子固体電解質型燃料電池用電極は、実施例4とともに電極特性が優れていることが判る。

【0031】

【発明の効果】本発明の第1の態様は、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と攪水性樹脂による触媒層が、ガス拡散層上に形成される高分子固体電解質型燃料電池用電極に於いて、前記触媒層とガス拡散層との間に、中間層を設けたことを特徴とする高分子固体電解質型燃料電池用電極（請求項1）であり、本発明の第2の態様は、同様の高分子固体電解質型燃料電池用電極において、前記触媒層が近接する部分のガス拡散層の気孔率を10~50%としたことを特徴とする高分子固体電解質型燃料電池用電極（請求項3）である。

【0032】両態様は、燃料電池の触媒層が担持触媒とともにガス拡散層中にしみ込んで又は進入して触媒活性が低下するとともにガス拡散層のガス拡散能が低下することを防止して触媒活性を最大限に利用することを意図するものである。触媒層とガス拡散層の間に位置する中間層及びその組織が緻密である気孔率が10~50%であるガス拡散層の触媒層側表面とも、触媒層のガス拡散層中への進入を困難にし、触媒層の触媒を活性が維持される本来の存在位置に保持しかつガス拡散層の目詰まりによるガス拡散の阻害ひいては反応効率の低下を防止するものである。前記中間層はガス拡散層の材質と同じでも異なっても良いが、カーボンとイオン交換樹脂又はカーボンとイオン交換樹脂と攪水性樹脂からなるものであることが好ましい（請求項2）。

【0033】又触媒層側表面の気孔率が10~50%である前記ガス拡散層は触媒層側に向かうほど気孔率を小さくする、換言すると気孔率に勾配を持たせることができ（請求項4）、これによりガス拡散能の確保と触媒層のガス拡散層の進入の抑制を更に好適に達成できる。本発明の第3の態様は、同様の高分子固体電解質型燃料電池

用電極に於いて、触媒に用いた2種類以上の貴金属又は貴金属合金が電極の厚み方向で種類が異なるように配置したものである（請求項5）。本態様では、使用する2種類の貴金属又は貴金属合金がそれぞれの有する機能を別個に発揮することにより従来達成不可能であった触媒の性能を最大限活用し触媒利用率の向上が可能になる。

【0034】例えば本態様は燃料電池のアノード用として好適に使用でき（請求項6）、触媒層のガスの拡散層側の白金及び／又はルテニウム触媒濃度が高くなるように配置され、かつ前記触媒層の膜側の白金系合金触媒濃度が高くなるように配置されて、触媒層の厚さ方向で触媒となる貴金属又は貴金属合金の種類が異なるように配置してある。この電極では、ガス拡散層側から供給される燃料がまずCO吸着能が優れた白金及び／又はルテニウム触媒に接触し、その後燃料電池反応を促進する白金系合金触媒と接触するため該白金系合金触媒を被毒するCO濃度が低下した燃料が触媒層において反応に関与するため触媒被毒量が従来と比較して大幅に減少し、効率的な燃料電池反応を進行させることができる。前記CO吸着除去用の白金及び／又はルテニウム触媒はCO吸着除去能に優れ燃料電池反応の進行に関してはその触媒作用は白金系合金触媒より劣るが、仮に白金系合金触媒が前記白金及び／又はルテニウム触媒の代わりに存在しても反応ポイントよりかなり離れているため反応に対する寄与は僅かであり、本発明によるCO吸着除去による反応への寄与の方が遙かに大きい。

【0035】本発明の第4の態様は、同様の高分子固体電解質型燃料電池用電極に於いて、触媒とイオン交換樹脂、又は触媒とイオン交換樹脂と攪水性樹脂を含む懸濁液を、電極基板上に塗布し、乾燥し、焼成することを複数回繰り返して電極触媒層を形成することを特徴とする高分子固体電解質型燃料電池用電極の製造方法である（請求項7）。本態様に従って異なる混合比率で構成された懸濁液を塗布すると（請求項8）、触媒層の厚さ方向に異なった触媒濃度又は構成要素濃度を有する触媒層を製造できる。又本方法に従って異なる原料を用いて構成された懸濁液を塗布すると（請求項9）、触媒層の厚さ方向に異なった種類の触媒金属等を有する触媒層を製造でき、換言すると触媒層の厚み方向でさまざまな要求に応じた最適な触媒層を形成することができ、電極特性に優れた電極を得ることができる。更に本態様では、1回に塗布する懸濁液の量が少なくなり、その膜厚が薄くなる為、乾燥時の収縮による歪みが小さく、従って大きなクラックが入りにくく、均一で歪みのない触媒層を製造できる。

【図面の簡単な説明】

【図1】本発明の高分子固体電解質型燃料電池用電極の一実施例を示す断面図。

【図2】本発明の高分子固体電解質型燃料電池用電極の他の実施例を示す断面図。

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【図3】従来の高分子固体電解質型燃料電池用電極の一例を示す断面図。

【図4】従来の高分子固体電解質型燃料電池用電極の他の例を示す断面図。

【図5】実施例1と比較例1の電極の電圧と電流密度との関係を測定したグラフ。

【図6】実施例2と比較例2の電極の電圧と電流密度との関係を測定したグラフ。

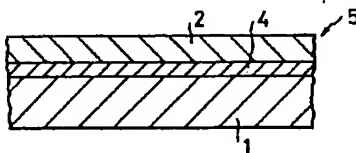
【図7】実施例3、比較例3及び比較例4の電極の電圧と電流密度との関係を測定したグラフ。

【図8】実施例4及び実施例5の電極の電圧と電流密度との関係を測定したグラフ。

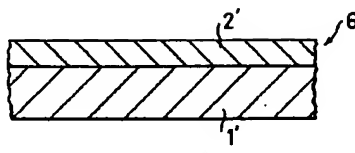
【符号の説明】

1、1'・・・ガス拡散層 2、2'・・・触媒層 4  
・・・中間層 5、6・・・電極

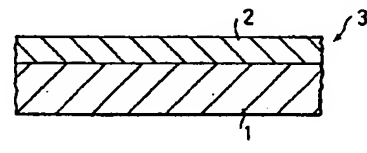
【図1】



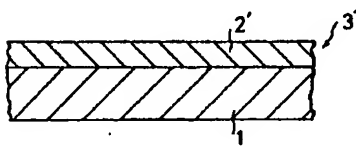
【図2】



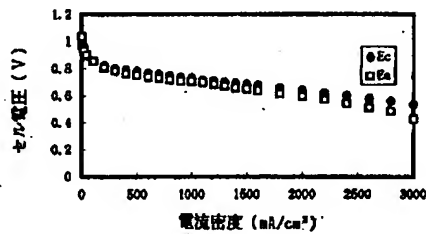
【図3】



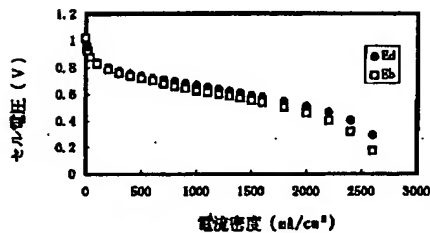
【図4】



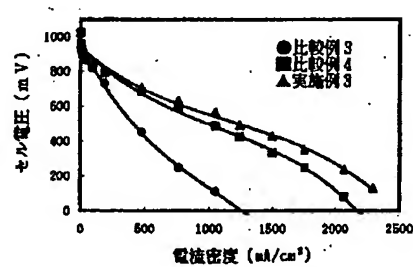
【図5】



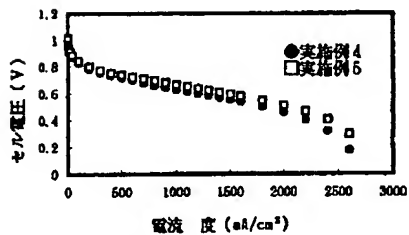
【図6】



【図7】



【図8】



## フロントページの続き

(71)出願人 391016716

ストーンハルト・アソシエーツ・インコーポ  
レーテッドSTONEHART ASSOCIATE  
S INCORPORATEDアメリカ合衆国 06443 コネチカット州、  
マジソン、コテッジ・ロード17、ビー・オ  
ー・ボックス1220

(72)発明者 多田 智之

神奈川県平塚市新町2番73号 田中貴金属  
工業株式会社技術開発センター内

(72)発明者 山本 夕美

神奈川県平塚市新町2番73号 田中貴金属  
工業株式会社技術開発センター内



DERWENT-ACC-NO: 1997-518608

DERWENT-WEEK: 199748

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TITLE: Electrode for solid polymer electrolyte type fuel  
battery - has interface layer set up between catalyst  
layer and gaseous diffusion layer

PATENT-ASSIGNEE: STONEHART ASSOC INC[STONN],  
TANAKA KIKINZOKU KOGYO  
KK[TANI], WATANABE M[WATAI]

PRIORITY-DATA: 1996JP-0082105 (March 11, 1996)

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H01M 004/86		008

APPLICATION-DATA:

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APPL-DATE		
JP 09245801A	N/A	1996JP-0082105
11, 1996		March

INT-CL (IPC): H01M004/86, H01M004/88, H01M004/92,  
H01M008/02,  
H01M008/10

ABSTRACTED-PUB-NO: JP 09245801A

BASIC-ABSTRACT:

The electrode (5) includes a catalyst layer (2) formed on a gaseous diffusion layer (1). The catalyst layer includes catalyst, ion exchange resin and water repellent resin. An interface layer (4) is set up between the catalyst layer and gaseous diffusion layer.

ADVANTAGE - Improves the utilisation factor of the catalyst.

CHOSEN-DRAWING: Dwg.1/8

TITLE-TERMS: ELECTRODE SOLID POLYMER  
ELECTROLYTIC TYPE FUEL BATTERY INTERFACE  
LAYER SET UP CATALYST LAYER GAS DIFFUSION  
LAYER

DERWENT-CLASS: A85 L03 X16

CPI-CODES: A12-E06A; A12-M; L03-E04B;

EPI-CODES: X16-C01C; X16-E06A;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; P0000 ; K9621\*R

Polymer Index [1.2]

018 ; ND01 ; K9745\*R ; Q9999 Q7341 Q7330 ; Q9999 Q7409  
Q7330 ; K9416

; K9698 K9676 ; K9483\*R

Polymer Index [1.3]

018 ; Q9999 Q7772

Polymer Index [2.1]

018 ; P0000

Polymer Index [2.2]

018 ; ND01 ; K9745\*R ; Q9999 Q7341 Q7330 ; Q9999 Q7409  
Q7330 ; K9416

; K9698 K9676 ; K9483\*R

Polymer Index [2.3]

018 ; B9999 B3509 B3485 B3372

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1997-165349

Non-CPI Secondary Accession Numbers: N1997-431730

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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## CLAIMS

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[Claim(s)]

[Claim 1] The electrode for solid-polymer-electrolyte type fuel cells characterized by the catalyst bed by the catalyst, ion exchange resin or a catalyst and ion exchange resin, and the water-repellent resin preparing an interlayer between the aforementioned catalyst bed and a gaseous diffusion layer in the electrode for solid-polymer-electrolyte type fuel cells formed on the gaseous diffusion layer.

[Claim 2] The electrode for solid-polymer-electrolyte type fuel cells according to claim 1 characterized by being what an interlayer becomes from carbon, ion exchange resin or carbon and ion exchange resin, and a water-repellent resin.

[Claim 3] The electrode for solid-polymer-electrolyte type fuel cells characterized by making into 10 - 50% the porosity of the gaseous diffusion layer of the portion to which the catalyst bed by the catalyst, ion exchange resin or a catalyst and ion exchange resin, and the water-repellent resin approaches the aforementioned catalyst bed in the electrode for solid-polymer-electrolyte type fuel cells formed on the gaseous diffusion layer.

[Claim 4] The electrode for solid-polymer-electrolyte type fuel cells according to claim 3 characterized by making the porosity of a gaseous diffusion layer small toward a catalyst bed side.

[Claim 5] The electrode for solid-polymer-electrolyte type fuel cells to which two or more kinds of the noble metals or the precious alloys which are used for a catalyst are characterized by being arranged so that kinds may differ in the thickness direction of a catalyst bed in the electrode for solid-polymer-electrolyte type fuel cells which consisted of a catalyst, ion exchange resin or a catalyst and ion exchange resin, and a water-repellent resin.

[Claim 6] The electrode for solid-polymer-electrolyte type fuel cells according to claim 5 characterized by arranging platinum and/or a ruthenium catalyst at the gaseous diffusion layer side of a catalyst bed, arranging a platinum system alloy catalyst at the film side of a catalyst bed, and being used as an anode.

[Claim 7] The manufacture method of the electrode for solid-polymer-electrolyte type fuel cells which applies the suspension containing a catalyst, ion exchange resin or a catalyst and ion exchange resin, and a water-repellent resin on a gaseous diffusion layer, dries and is characterized by repeating calcinating two or more times and forming a catalyst bed in the manufacture method of the electrode for solid-polymer-electrolyte type fuel cells which consists of a catalyst, ion exchange resin or a catalyst and ion exchange resin, and a water-repellent resin.

[Claim 8] The manufacture method of the electrode for solid-polymer-electrolyte type fuel cells according to claim 7 characterized by at least one of the suspension repeatedly applied on a gaseous diffusion layer being the suspension which consisted of different mixed ratios.

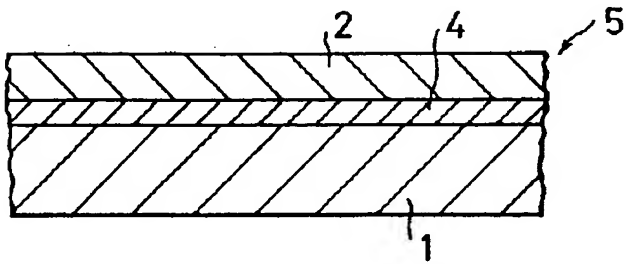
[Claim 9] The manufacture method of the electrode for solid-polymer-electrolyte type fuel cells according to claim 7 characterized by at least one of the suspension repeatedly applied on an electrode substrate being the suspension constituted using a different raw material.

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[Translation done.]

Drawing selection [Representative drawing] 

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[Translation done.]

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3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the aforementioned electrode for fuel cells which raised more the utilization factor of the catalyst of the aforementioned catalyst bed in the electrode for fuel cells which changes from a catalyst bed and a gaseous diffusion layer to a detail, and its manufacture method about the electrode for solid-polymer-electrolyte type fuel cells, and its manufacture method.

[0002]

[The conventional technology and a trouble] Since a fuel cell is efficient and the pollution-free power plant which use hydrogen and various fossil fuels, it has a great hope socially as a power plant of "postatomic power" which can cope with energy problems and a full-terrestrial pollution problem. Various fuel cells according to the use, such as an object for steam-generated alternative power generation, an object for the on-site power generation of a building or a works unit, or an object for space, are developed. In recent years, the acid rain by the greenhouse effect centering on carbon dioxide gas, NO<sub>x</sub>, SO<sub>x</sub>, etc. is recognized as serious pollution which threatens the future of the earth. Since one of the main sources of eccrisis of these pollution gas is internal combustion engines, such as an automobile, the tendency which uses a fuel cell as a motor power supply which replaces with the internal combustion engine for mount, and operates is increasing quickly. In this case, like many incidental facilities, the thing of a cell small as much as possible is desirable, and it is indispensable that for that the power density of the main part of a cell and output current density are high. The solid-polymer-electrolyte type fuel cell (it is called Following PEMFC) using ion exchange membrane as a candidate of a leading fuel cell who fulfills this condition attracts attention.

[0003] The electrode 3 of a fuel cell is manufactured by applying the paste which \*\*\*\*(ed) support which consists of the carbon black which supported the catalyst, or a carbon fiber to water or the organic solvent, and forming a catalyst bed (a reaction layer, electrode catalyst bed) 2 on the gaseous diffusion layer (electrode substrate) 1 which consists of carbonaceous material as shown in drawing 3. How since the reaction of a fuel cell occurs on the aforementioned catalyst, it uses the aforementioned catalyst effectively is the greatest factor which influences the amount of energy obtained by the aforementioned fuel cell. However, in the conventional fuel cell, the utilization factor of a catalyst cannot be made into the maximum for various reasons, but there is a fault that the expensive catalyst, especially the platinum metal catalyst cannot be used effectively. This invention persons reached the conclusion that they were the following reasons with three main points, as a result of considering carefully the reason for the ability not to aim at a deployment of the catalyst which exists in the catalyst bed of this fuel cell.

[0004] Since the 1st reason has the porosity of the conventional gaseous diffusion layer as high as about 60 - 80%, In case a catalyst bed including the catalyst which exists in the portion which faces or approaches the gaseous diffusion layer of a catalyst bed is electrode formation, it sinks in or advances into a gaseous diffusion layer. It is that a part of catalyst exists in a gaseous diffusion layer substantially, and as for this



catalyst, \*\*\*\* of a proton becomes difficult, as a result, this catalyst cannot be contributed to a reaction but the utilization factor of a catalyst falls. It is mentioned that the number of the catalysts which exist in a catalyst bed is one as the 2nd reason. For example, all are insufficient although the utilization of the catalyst for fuel cells which PEMFC has the trouble that it is tended poisoning of the catalyst of an anode electrode to carry out CO in fuel, for the low-temperature operability, and various alloy catalysts are proposed from the former, and has CO-proof poisoning nature is tried.

[0005] The fact that the catalyst concentration of a catalyst bed is uniform is cited as the 3rd reason. From the former, the catalyst bed of the electrode for solid-polymer-electrolyte type fuel cells applies at once the suspension which \*\*\*\*(ed) a catalyst, ion exchange resin or a catalyst and ion exchange resin, and the water-repellent resin into the mixed liquor of an organic solvent and water on an electrode substrate, it dries, and calcinates and is manufactured. In this method, since it applies at once, the hybrid raw material of a catalyst bed cannot be changed in the thickness direction of a catalyst bed, and the optimal catalyst bed according to each cannot be obtained in the thickness direction of a catalyst bed. The most produces the reaction of a fuel cell in the interface of a gaseous diffusion layer and a catalyst bed, in the catalyst bed of the fuel cell which the catalyst in the conventional catalyst bed distributes uniformly, the catalyst located distantly [ layer / gaseous diffusion ] can hardly be contributed to the aforementioned reaction, but the catalyst utilization factor is falling. Furthermore, by this method, in order to apply suspension on an electrode substrate at once, it has the fault that a catalyst bed may become thick and a big crack may enter in the middle of dryness.

[0006]

[Problem(s) to be Solved by the Invention] Then, this invention offers the electrode for solid-polymer-electrolyte type fuel cells which the catalyst in a catalyst bed advances into a gaseous diffusion layer the 1st, and does not lose the catalytic activity. this invention offers the electrode for solid-polymer-electrolyte type fuel cells which has CO-proof poisoning nature in the 2nd, and has activity also to the reaction of a fuel cell. this invention offers the electrode for solid-polymer-electrolyte type fuel cells which has [ 3rd ] the activity according to the thickness direction of a catalyst bed.

[0007]

[Means for Solving the Problem] The 1st mode of this invention for solving the above-mentioned technical problem is an electrode for solid-polymer-electrolyte type fuel cells characterized by preparing an interlayer between a catalyst bed and a gaseous diffusion layer so that the aforementioned catalyst bed sinks in or may not advance into a gaseous diffusion layer in the electrode for solid-polymer-electrolyte type fuel cells by which the catalyst bed by the catalyst, ion exchange resin or a catalyst and ion exchange resin, and the water-repellent resin was formed on the gaseous diffusion layer. The 2nd mode of this invention is an electrode for solid-polymer-electrolyte type fuel cells characterized by making into 10 - 50% the porosity of the gaseous diffusion layer of the portion which a catalyst bed approaches in the same electrode for solid-polymer-electrolyte type fuel cells.

[0008] The 3rd mode of this invention is the electrode for solid-polymer-electrolyte type fuel cells characterized by arranging the kind of two or more kinds of noble metals used as a catalyst, or precious alloy so that kinds may differ in the thickness direction of an electrode, especially an electrode for anodes in the same electrode for solid-polymer-electrolyte type fuel cells. The 4th mode of this invention is the manufacture method of the electrode for solid-polymer-electrolyte type fuel cells which the suspension which \*\*\*\*(ed) a catalyst, ion exchange resin or a catalyst and ion exchange resin, and the water-repellent resin into the mixed liquor of the organic solvent, water, etc. is applied on an electrode substrate, and dries, repeats calcinating two or more times and forms an electrode catalyst bed in the same electrode for solid-polymer-electrolyte type fuel cells.

[0009] this invention is explained in detail below. It is going to prevent that the catalyst in a catalyst bed advances into a gaseous diffusion layer, and each of 1st mode of the above and 2nd mode loses catalytic activity. the catalyst effect which promotes a fuel cell reaction only after exists in a catalyst bed is generated,

and if the catalyst in a catalyst bed exists in a gaseous diffusion layer, it has only the function to check gaseous diffusion and to block supply of the reactant gas to the aforementioned catalyst bed, and occurs of generation gas, as mentioned above. Therefore, if penetration into the gaseous diffusion layer of a catalyst bed the catalyst which exists in a catalyst bed, or own can be prevented, the utilization factor of a catalyst will improve certainly. Therefore, in this invention, an interlayer is formed between a catalyst bed and a gaseous diffusion layer so that the porosity of the gaseous diffusion layer which touches a catalyst bed may be made low, and penetration of a catalyst may be suppressed or the aforementioned catalyst bed may not sink in into a gaseous diffusion layer, or so that it may not advance.

[0010] Although the porosity of the gaseous diffusion layer of the usual fuel cell is about 60 - 80%, the aperture formed in a gaseous diffusion layer is made small, and it is made for a catalyst bed not to advance by making this porosity low with 10 - 50% in this invention. If it exceeds 50%, the porosity of the usual gaseous diffusion layer will become almost equivalent, and the reason for having made porosity into 10 - 50% is because a reaction will be conversely checked at less than 10% since the gaseous diffusion function which is a function of original of a gaseous diffusion layer is spoiled and it becomes impossible to perform smoothly supply of reactant gas, and occurs of generation gas, and is because there are few improvement effects of penetration prevention of the aforementioned catalyst. If penetration prevention of this catalyst is performed only in the portion of the comparatively slight thickness which touches the catalyst bed of a gaseous diffusion layer, it is enough, and it is desirable that making it so small that it going to a catalyst bed side etc. carries out the porosity of a gaseous diffusion layer, and the gaseous diffusion ability of a gaseous diffusion layer is made not to be spoiled.

[0011] The size of the aforementioned porosity can be adjusted according to the conditions of the hotpress at the time of gaseous diffusion layer manufacture etc., and in order to manufacture a gaseous diffusion layer with small porosity, it should just enlarge the pressure of a hotpress. What is necessary is to prepare the gaseous diffusion layer of \*\*\*\* which is different in porosity two or more sheets, and just to join them mutually, in order to manufacture the gaseous diffusion layer to which porosity became small so that it goes to a catalyst bed. Next, the above-mentioned interlayer is prepared for making this interlayer achieve a function equivalent to the portion of the above-mentioned gaseous diffusion layer which made porosity small which approaches a catalyst bed at least. Although it is desirable to make it small as for the porosity so that a catalyst bed may not advance into this interlayer, even if a part advances, it is not connected so much with the inaction, but if an interlayer can prevent that a catalyst bed and a gaseous diffusion layer contact directly, the function will be attained, and this interlayer's porosity can be made into about 10 - 80% of latus range, and is desirable. [ about 20 - 60% of ] Even if this interlayer's porosity is 80%, in order that a catalyst bed may not advance into a direct gaseous diffusion layer, the rate of the catalyst bed which advances to a gaseous diffusion layer by existence of this interlayer decreases greatly, and it contributes to the improvement in a utilization factor of a catalyst.

[0012] Even if it makes the aforementioned interlayer's quality of the material be the same as that of the quality of the material of a gaseous diffusion layer, other quality of the materials which have a similar property are sufficient as it, and it is desirable that it is what consists of carbon, ion exchange resin or carbon and ion exchange resin, and a water-repellent resin. In the 1st of this invention, and the 2nd mode, the catalyst in the catalyst bed of a fuel cell advances into a gaseous diffusion layer, the substantial amount of catalysts hardly decreases, and the deployment can be aimed at. In the 3rd mode of this invention, it has the intention of raising a catalyst utilization factor by carrying out the maximum practical use of the performance of the catalyst of a catalyst bed by using two or more kinds such as the noble metals which constitute a catalyst bed, or its alloy. The function may change with the existence positions also with the catalyst which exists in the same catalyst bed. In the electrode, especially anode of a fuel cell, there is a function to adsorb the function which promotes the reaction of a fuel cell for an electrode catalyst, and CO to which it mixes into fuel, the aforementioned catalyst is supplied, poisoning of the anode is carried out, and the reaction activity of an

anode is reduced, and to remove out of fuel.

[0013] For example, as a catalyst of a fuel cell reaction, a platinum system alloy has a platinum catalyst and a desirable ruthenium catalyst as an object for CO adsorption. Although only one kind of noble metals or its alloy was mostly distributed by homogeneity at the catalyst bed of the conventional electrode for fuel cells and one kind of precious alloy catalyst effective also in the adsorption treatment of CO effective in a fuel cell reaction has been investigated, the precious alloy catalyst with which are satisfied of both functions is not found out. In the 3rd mode of the above of this invention, it separates from the conventional fundamental view of achievement of two or more kinds of functions by one kind of these noble metals, or the precious alloy catalyst, and the catalyst for fuel cells, especially anode catalyst with which can be satisfied of the whole of each function are offered by using together two or more the optimal noble metals or the precious alloy catalysts over each function.

[0014] For example, in the case of the anode for fuel cells which means promotion of a fuel cell reaction, and achievement of both the functions of the adsorption treatment of CO in fuel, among catalyst beds, a platinum catalyst or a ruthenium catalyst is used, the adsorption treatment of CO in adsorption fuel is mainly performed to the side near a gaseous diffusion layer in this catalyst bed, a platinum system alloy catalyst is used for the side near a film among catalyst beds, and a fuel cell reaction is promoted in this catalyst bed. That is, fuel was not supplied to a catalyst bed through the gaseous diffusion layer of an anode, oxidation reaction of hydrogen gas did not occur near the aforementioned gaseous diffusion layer of this catalyst bed, and the film of an opposite side, and the portion with the same catalyst bed near a gaseous diffusion layer has not necessarily contributed to oxidation reaction of the hydrogen gas which happens near the film so much. Therefore, the synergistic effect that CO in the fuel supplied to an anode is removable arises, without decreasing most catalyst effects of the whole anode, if platinum and the ruthenium of CO effective for an adsorption treatment which were mentioned above, for example are supported, although it is not so effective in hydrogen gas oxidization in the catalyst metal of the portion near the gaseous diffusion layer in this catalyst bed. That is, since it is easy to stick to a platinum catalyst or a ruthenium catalyst first, CO supplied to an anode electrode in connection with fuel sticks to this. If an adsorption equilibrium is reached here, although adsorption will progress to the catalyst of a platinum system alloy, CO which reaches to the catalyst of the side near films, such as a platinum system alloy, according to the screen effect in the field of a platinum catalyst or a ruthenium catalyst decreases, and the rate of CO poisoning decreases. Therefore, it becomes the electrode which is excellent in CO-proof nature, without reducing the performance of the catalyst which promotes the fuel cell reaction of the side near a film.

[0015] By two or more kinds, although there is no limitation, it usually makes two kinds the kind of the noble metals which were mentioned above and to be used or precious alloy, and you may make it constitute a cathode similarly in addition to an anode. Moreover, two or more [ above ] noble metals or a precious alloy is arranged so that two or more noble metals or precious alloys may exist in the thickness direction of a catalyst bed in layers that is,. In addition, the interface between metals does not need to be divided strictly and two or more kinds of noble metals or precious alloys may be intermingled near an interface. the catalyst bed containing the two or more aforementioned kinds of noble metals or precious alloys producing two or more catalyst bed precursors containing one kind of noble metals, or a precious alloy, and joining these -- or it can manufacture by applying and calcinating the suspension containing other noble metals or precious alloys on the front face of the 1st catalyst precursor only containing the noble metals or the precious alloy produced beforehand, and forming the 2nd catalyst precursor in it etc.

[0016] The 4th mode of this invention is suitable for manufacture of the catalyst bed to which two or more kinds such as the noble metals which constitute a catalyst bed without a big crack or a catalyst bed, or its alloy were used in the direction of layer thickness with respect to the manufacture method of the electrode for solid-polymer-electrolyte type fuel cells, or the concentration of one kind of noble metals or the direction of layer thickness of a precious alloy was changed. Although the catalyst bed of the conventional fuel cell is

manufactured by applying at once the support which supported the catalyst, and the suspension which kneaded the fluororesin etc., and calcinating it on a gaseous diffusion layer, by this method, the amount of suspension applied at once on a gaseous diffusion layer increases, distortion by the contraction at the time of baking and dryness becomes large, it is easy to produce a big crack, and it tends to be connected with the liquid spill and gas leakage at the time of using it as a fuel cell. If it calcinates by on the other hand dividing and applying suspension to multiple times like this invention, since the amount of the suspension applied at once will decrease and the thickness will become thin, a crack with it cannot enter easily, it is uniform and a catalyst bed without distortion can be manufactured. [ the small therefore distortion by the contraction at the time of dryness and ] [ big ]

[0017] Moreover, various functions demanded in the thickness direction of the electrode catalyst bed obtained can be made to have by carrying out the multiple-times application of the suspension using a different mixed ratio (composition) or a different raw material. For example, many catalysts can be arranged to a film side, many ion exchange resin can be arranged, consequently a deployment of a catalyst, and \*\*\*\* and the gaseous diffusion function of a proton improve, and it becomes what was excellent at the electrode characteristic. It is useful also to manufacture of the catalyst bed which has two or more noble metals or precious alloys which are the 3rd mode of this invention mentioned above further, for example. The number of times to apply is because workability is bad and serves as cost quantity, while the above effect cannot be desired more, if about 6 times is desirable and exceeds 6 times twice or more.

[0018]

[Example] Although the example of the electrode for solid-polymer-electrolyte type fuel cells of this invention and its manufacture method is explained with the example of comparison, these do not limit this invention.

[The example 1 of comparison] the gaseous diffusion layer 1 which shows the paste which was mixed for 50 minutes and obtained 20g of concentration liquid and 6g of distilled water of 2g of Pt50% support catalysts, and 5% (tradename Nafion) solution of ion exchange resin with the planet ball mill to drawing 3 of 80% of porosity by the bar coat method -- applying -- 60 degrees C -- for 10 minutes -- drying -- further -- it calcinated for 1 minute by 130 \*\* and 20 kg/cm<sup>2</sup>, the catalyst bed 2 was formed, and the electrode 3 was

[0019]

[Example 1] In the electrode which consists of the same catalyst bed 2 as the example 1 of comparison, and a gaseous diffusion layer 1 beforehand between a catalyst bed 2 and the gaseous diffusion layer 1 The paste which was mixed for 50 minutes and obtained 15g of concentration liquid and 10g of distilled water of carbon 2g and 5% (tradename Nafion) solution of ion exchange resin with the planet ball mill as shown in drawing 1 is made to intervene. if it puts in another way, this paste will be applied to the gaseous diffusion layer 1, and 60 degrees C will dry for 10 minutes -- it calcinated for 1 minute by 130 degree C and 20 kg/cm<sup>2</sup>, the interlayer 4 was formed, the aforementioned catalyst bed 2 was formed on this interlayer 4 the appropriate back, and the electrode 5 was obtained

[0020] When the relation between voltage and current density was measured on condition that the hydrogen gas of the cell temperature of 80 degrees C, and two atmospheric pressure, and the oxygen gas of three atmospheric pressure using the electrode of the example 1 of comparison and the electrode of an example 1 which were manufactured as mentioned above, the result as shown in the graph of drawing 5 was obtained. It turns out that the electrode (Ec) of an example 1 excels the electrode (Ea) of the example 1 of comparison in the electrode characteristic so that it may understand in this graph. A catalyst bed does not sink [ the electrode of an example 1 ] into a gaseous diffusion layer by existence of an interlayer, and the amount of catalysts does not decrease, but this can be conjectured to be because for the catalyst to have been used effectively.

[0021]

[The example 2 of comparison] 10g of concentration liquid and 4g of distilled water of 1.43g of Pt30% support catalysts, and 5% (tradename Nafion) solution of ion exchange resin it applies to the gaseous diffusion layer 1 which shows the paste which mixed for 50 minutes and was obtained with the planet ball

mill to drawing 4 of 80% of porosity by the bar coat method, and 60 degrees C dries for 10 minutes -- it calcinated for 1 minute by 130 degree C and 20 kg/cm<sup>2</sup>, catalyst bed 2' was formed, and electrode 3' was obtained

[0022]

[Example 2] it applies to gaseous diffusion layer 1' which shows the same paste as the example 2 of comparison to drawing 2 of about 33% of porosity by the bar coat method, and 60 degrees C dries for 10 minutes -- it calcinated for 1 minute by 130 degree C and 20 kg/cm<sup>2</sup>, catalyst bed 2' was formed, and the electrode 6 was obtained When the relation between voltage and current density was measured for the cell temperature of 80 degrees C, hydrogen gas, and oxygen gas on condition that the ordinary pressure using the electrode of the example 2 of comparison and the electrode of an example 2 which were constituted as mentioned above, the result as shown in the graph of drawing 6 was obtained. It turns out that the electrode (Ed) of an example 2 excels the electrode (Eb) of the example 2 of comparison in the electrode characteristic so that it may understand in this graph. A catalyst bed does not sink [ the electrode of an example 2 ] into the gaseous diffusion layer of a blinding state, and the amount of catalysts does not decrease, but this can be conjectured to be because for the catalyst to have been used effectively.

[0023]

[The example 3 of comparison] The planet ball mill ground 1.43g of Pt30% support catalysts, 10g of concentration liquid of 5% (tradename Nafion) solution of ion exchange resin, and 4g of distilled water, and it agitated, mixed, and the paste was made, this paste was applied on the electrode substrate of a carbon paper, was dried and calcinated, the 40-micrometer catalyst bed was formed, and the anode electrode was obtained.

[0024]

[The example 4 of comparison] Pt-Mo33% support catalyst The planet ball mill ground 1.5g, 10g of concentration liquid of a Nafion 5% solution, and four cc of distilled water, and it agitated, mixed, and the paste was made, this paste was applied on the electrode substrate of a carbon paper, was dried and calcinated, the 40-micrometer catalyst bed was formed, and the anode electrode was obtained.

[0025]

[Example 3] 1.43g of Pt30% support catalysts, 10g of concentration liquid of 5% (tradename Nafion) solution of ion exchange resin, A planet ball mill grinds 4g of distilled water, agitate, mix, and the 1st paste is made. Moreover, Pt-Mo33% support catalyst 1.5g, 10g of concentration liquid of 5% (tradename Nafion) solution of ion exchange resin, A planet ball mill grinds four cc of distilled water, agitate, mix, and the 2nd paste is made. And it calcinated, the 1st 10-micrometer catalyst bed was formed, the 2nd paste was applied on it, it dried, and the 1st paste is applied on the electrode of a carbon paper, and the anode electrode was obtained [ it dries and / it calcinated, the 2nd 30-micrometer catalyst bed was formed, and ].

[0026] It is CO 100ppm at the cell temperature of 80 degrees C about the anode electrode of the examples 3 and 4 of these comparison, and an example 3. When the hydrogen gas and oxygen gas which are included were supplied in 1l. / min, and the ordinary pressure, respectively and the relation between voltage and current density was measured, the result as shown in the graph of drawing 7 was obtained. It turns out that the anode electrode of an example 3 excels the anode electrode of the examples 3 and 4 of comparison in the electrode characteristic so that it may understand in the graph of drawing 7 . This is adsorbed in CO by the 1st catalyst bed, and the anode electrode of an example 3 can surmise that it is because it became the electrode which CO which reaches the 2nd catalyst bed decreased, and the rate of CO poisoning decreased, and was excellent in CO-proof nature.

[0027]

[The example 5 of comparison] It printed, churning mixture of 10g of concentration liquid and 4g of distilled water of 1.43g of Pt30% support catalysts and 5% (tradename Nafion) solution of ion exchange resin was carried out for 50 minutes with the planet ball mill, the paste was made, it dried and this paste was calcinated so that it might become the amount of Pt support of 1 mg/cm<sup>2</sup> at a time on the electrode substrate of a carbon

paper, and the electrode for solid-polymer-electrolyte type fuel cells was obtained.

[0028]

[Example 4] The same paste as the example 5 of comparison was made, on the electrode substrate of a carbon paper, this paste was printed, was dried and calcinated in 3 steps, the catalyst bed of the amount of support of Pt1 mg/cm<sup>2</sup> was formed, and the electrode for solid-polymer-electrolyte type fuel cells was obtained.

[0029]

[Example 5] Carry out churning mixture of 6g of concentration liquid and 7g of distilled water of 1.43g of Pt30% support catalysts, and 5% (tradename Nafion) solution of ion exchange resin for 50 minutes with a planet ball mill, and the 1st paste is made. Moreover, the same paste as the example 5 of comparison was made as the 2nd paste, on the electrode substrate of a carbon paper, these 1st pastes and the 2nd paste were printed a total of 4 times by a unit of 2 times, were dried and calcinated, the catalyst bed was formed, and the electrode for solid-polymer-electrolyte type fuel cells was obtained.

[0030] Although the thing of the example 5 of comparison had partial ablation when these electrodes for solid-polymer-electrolyte type fuel cells were inspected, the thing of examples 4 and 5 did not have ablation and did not have a big crack, either. A result with which the thing of the example 5 of comparison cannot measure the cell temperature of 80 degrees C, hydrogen gas, and oxygen gas at all, but the thing of an example 4 and an example 5 indicates it to be for them to the graph of drawing 8 when the relation between the voltage of these electrodes for solid-polymer-electrolyte type fuel cells and current density is measured on condition that 1l. / min, and an ordinary pressure, respectively was obtained. It turns out that the electrode for solid-polymer-electrolyte type fuel cells of an example 5 is excellent in the electrode characteristic with the example 4 so that it may understand in the graph of drawing 8.

[0031]

[Effect of the Invention] In the electrode for solid-polymer-electrolyte type fuel cells by which the catalyst bed according [ the 1st mode of this invention ] to a catalyst, ion exchange resin or a catalyst and ion exchange resin, and a water-repellent resin is formed on a gaseous diffusion layer between the aforementioned catalyst bed and a gaseous diffusion layer It is the electrode for solid-polymer-electrolyte type fuel cells (claim 1) characterized by preparing an interlayer. the 2nd mode of this invention In the same electrode for solid-polymer-electrolyte type fuel cells, it is the electrode for solid-polymer-electrolyte type fuel cells (claim 3) characterized by making into 10 - 50% the porosity of the gaseous diffusion layer of the portion which the aforementioned catalyst bed approaches.

[0032] Both modes mean preventing that the gaseous diffusion ability of a gaseous diffusion layer falls, and making the most of catalytic activity while the catalyst bed of a fuel cell sinks in into a gaseous diffusion layer with a support catalyst, or advances and catalytic activity falls. The catalyst bed side front face of the gaseous diffusion layer whose precise porosity is 10 - 50% makes difficult penetration into the gaseous diffusion layer of a catalyst bed, and the interlayer located between a catalyst bed and a gaseous diffusion layer and its organization hold the catalyst of a catalyst bed in the original's existence position where activity is maintained, and prevention \*\*\*\*\* of the gaseous diffusion by the blinding of a gaseous diffusion layer prevents decline in reaction efficiency. although the aforementioned interlayer may differ even if they are the same as the quality of the material of a gaseous diffusion layer, it is desirable that it is what consists of carbon, ion exchange resin or carbon and ion exchange resin, and a water-repellent resin (claim 2)

[0033] Moreover, if porosity is made small and put in another way so that the aforementioned gaseous diffusion layer whose porosity of a catalyst bed side front face is 10 - 50% goes to a catalyst bed side, it can give inclination to porosity (claim 4) and, thereby, can attain still more suitably reservation of gaseous diffusion ability, and suppression of penetration of the gaseous diffusion layer of a catalyst bed. In the same electrode for solid-polymer-electrolyte type fuel cells, two or more kinds of the noble metals or the precious alloys which were used for the catalyst arrange the 3rd mode of this invention so that kinds may differ in the thickness direction of an electrode (claim 5). In this mode, when two kinds of noble metals or the precious



alloy to be used demonstrates separately each function which it has, the maximum practical use of the performance of the catalyst which was not able to be attained conventionally is carried out, and improvement in a catalyst utilization factor is attained.

[0034] For example, this mode can be suitably used as an object for the anodes of a fuel cell (claim 6), it is arranged so that the platinum and/or ruthenium catalyst concentration by the side of the diffusion layer of the gas of a catalyst bed may become high, and it is arranged so that the platinum system alloy-catalyst concentration by the side of the film of the aforementioned catalyst bed may become high, and it is arranged so that the kinds of the noble metals which serve as a catalyst in the thickness direction of a catalyst bed, or precious alloy may differ. Since the fuel with which CO concentration which carries out poisoning of this platinum system alloy catalyst in order to contact the platinum system alloy catalyst to which the fuel supplied from a gaseous diffusion layer side contacts the platinum and/or the ruthenium catalyst in which CO adsorption capacity was excellent first, and promotes a fuel cell reaction after that in this electrode fell participates in a reaction in a catalyst bed, the amount of catalyst poisoning can decrease sharply as compared with the former, and an efficient fuel cell reaction can be advanced. Although the platinum and/or the ruthenium catalyst for the aforementioned CO adsorption treatments are excellent in CO adsorption-treatment ability and the catalysis is inferior to a platinum system alloy catalyst about advance of a fuel cell reaction, since it is considerably separated from the reaction point even if it exists instead of platinum system alloy catalysts being the aforementioned platinum and/or a ruthenium catalyst temporarily, the contribution to a reaction is slight and its contribution to the reaction by CO adsorption treatment by this invention is larger for whether it being \*\*.

[0035] The suspension which contains a catalyst, ion exchange resin or a catalyst and ion exchange resin, and a water-repellent resin in the same electrode for solid-polymer-electrolyte type fuel cells is applied on an electrode substrate, and the 4th mode of this invention dries and is the manufacture method of the electrode for solid-polymer-electrolyte type fuel cells characterized by repeating calcinating two or more times and forming an electrode catalyst bed (claim 7). If the suspension which consisted of different mixed ratios according to this mode is applied (claim 8), the catalyst bed which has the different catalyst concentration or different component concentration in the thickness direction of a catalyst bed can be manufactured. The catalyst bed which has the catalyst metal of a different kind in the thickness direction of a catalyst bed etc. when the suspension constituted using a different raw material according to the \*\*\*\* method is applied (claim 9) can be manufactured, if it puts in another way, the optimal catalyst bed according to various demands can be formed in the thickness direction of a catalyst bed, and the electrode excellent in the electrode characteristic can be obtained. Furthermore, in this mode, since the amount of the suspension applied at once decreases and the thickness becomes thin, a crack with it cannot enter easily, it is uniform and a catalyst bed without distortion can be manufactured. [ the small therefore distortion by the contraction at the time of dryness and ] [ big ]

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[Translation done.]